



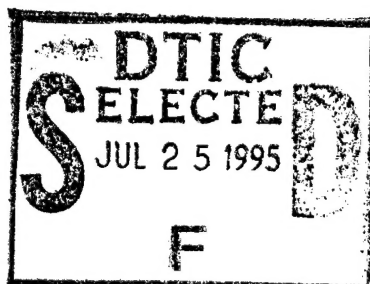
EDGEWOOD

RESEARCH, DEVELOPMENT & ENGINEERING CENTER

U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

ERDEC-TR-239

SMOKE FROM LONG CHAIN ALCOHOLS



William E. White

RESEARCH AND TECHNOLOGY DIRECTORATE

Ronald S. Grieb

GEO-CENTERS, INC.
Fort Washington, MD 20744

May 1995

Approved for public release; distribution is unlimited.



Aberdeen Proving Ground, MD 21010-5423

19950724 063

DTIC QUALITY INSPECTED 5

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302 and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE 1995 May	3. REPORT TYPE AND DATES COVERED Final, 94 Apr - 94 Oct	
4. TITLE AND SUBTITLE Smoke From Long Chain Alcohols			5. FUNDING NUMBERS None	
6. AUTHOR(S) White, William E. (ERDEC); and Grieb, Ronald S. (GEO-Centers, Inc.)				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) DIR, ERDEC, ATTN: SCBRD-RTB, APG, MD 21010-5423 GEO-Centers, Inc., Fort, Washington, MD 20744			8. PERFORMING ORGANIZATION REPORT NUMBER ERDEC-TR-239	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)			10. SPONSORING / MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) A fuel composed principally of C ₁₁ to C ₁₄ hydrocarbons, JP-8, is too volatile to produce a persistent smoke cloud. Gas phase catalytic oxidation of the hydrocarbon components would yield new compounds (alcohols, carboxylic acids, and diols) that have lower vapor pressures. This report describes experiments to determine the merit of long chain alcohols for obscuration. Dodecanol (C ₁₂) produced effective smoke at ambient temperatures but was ineffective above 100 °F. Decanol (C ₁₀) was less effective at ambient temperatures. Thus, it appears that the oxidation products of the C ₁₁ through C ₁₄ components in JP-8 will be useful for obscuration purposes. The program now shifts to identifying catalysts to effect the required oxidation without consuming the entire carbon chain.				
14. SUBJECT TERMS JP-8 Aerosol Smoke Dodecanol Alcohol Oxidation			15. NUMBER OF PAGES 48	
			16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL	

Blank

PREFACE

The work described in this report was supported by the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC) Skunk Works Program. This work was started in April 1994 and completed in October 1994.

The use of trade or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for public release. Registered users should request additional copies from the Defense Technical Information Center; unregistered users should direct such requests to the National Technical Information Service.

Acknowledgments

The author expresses his appreciation to members of the ERDEC Technical Library for valuable assistance during the initial concept development and planning stages. Corky Smith conducted literature searches on a wide variety of topics, and Carolyn Sullivan obtained background information expeditiously via the interlibrary loan program. The author also thanks Beth Hirsh, ERDEC Environmental Office, for preparing the environmental assessment and for overseeing its progress through the approval chain; Tom Rosso, ERDEC Analytical Chemistry Team, for performing the GC/MS analyses; and Mark Guelta, Horace Pearce, Dr. Edward Stuebing, and Dr. Janon Embry for valuable consultive assistance.

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification _____	
By _____	
Distribution /	
Availability Codes	
Dist	Avail and/or Special
A-1	

Blank

CONTENTS

1. INTRODUCTION	9
2. BACKGROUND	9
2.1 Meetings and Identification of Problem	9
2.2 Previous Attempts to Modify Fuels	11
3. THEORETICAL EVALUATION	12
3.1 JP-8 Composition	12
3.2 Research Approach for Reducing Volatility of Hydrocarbons	15
3.3 Objective of Smoke Generation Experiments	18
3.4 Choices for Design of Smoke/Obscuration Experiments	18
4. EQUIPMENT	19
4.1 Chemicals	19
4.2 Aerosol Measurements	19
4.3 Aerosol Generation	20
4.4 Smoke Containment	20
5. EXPERIMENTAL PROCEDURES	21
5.1 Data Reduction	21
5.2 Chamber Procedures	21
5.3 Cloche Procedures	22
6. RESULTS	22
7. CONCLUSIONS	29
LITERATURE CITED	31
APPENDICES	
A1 Ethylene Glycol in 1 m ³ Chamber	35
A2 Rosco Fog Fluid in 1 m ³ Chamber	36
A3 Decanol in 1 m ³ Chamber	37
A4 Propylene Glycol in 1 m ³ Chamber	38

A5	Dodecanol - 1st Run in Cloche (T = 24 °C)	39
A6	Dodecanol - 2nd Run in Cloche (T = 21.5 °C)	40
A7	Emery 3002 in Cloche (T = 27 °C)	41
A8	Emery 3004 in Cloche (T = 24 °C)	42
A9	Dodecanol - 1st Run in Cloche (T = 39 °C)	43
A10	Dodecanol -2nd Run in Cloche (T = 39 °C).....	44
A11	Dodecanol - 3rd Run in Cloche (T = 41 °C)	45
A12	Emery 3004 in Cloche (T = 36 °C)	46
A13	Octanol in Cloche (T = 17 °C)	47
A14	n-Decanol in Cloche (T = 26 °C)	48

FIGURES

1	Boiling Points (°C) For a Series of Hydrocarbons (Alkanes), Primary Alcohols, Carboxylic Acids, and α,ω Diols	17
2	Persistency of Smoke in the 1 m ³ Chamber	23
3	Persistency of Dodecanol in the Cloche at Ambient Temperatures	24
4	Comparison of the Persistency in the Cloche of Dodecanol with Two Poly Alpha Olefins, Emery 3002 and Emery 3004	26
5	Persistency of Dodecanol and Emery 3004 at Higher Temperatures	27
6	Comparison of the Persistency in the Cloche of Lower Molecular Weight Alcohols	28

TABLES

1	Physical Properties of Liquid Smoke Materials	10
2	Chemical Structures	13

Blank

SMOKE FROM LONG CHAIN ALCOHOLS

1. INTRODUCTION

Fog oil, a mixture of hydrocarbons from the high boiling distillate, has been the principal smoke material for obscuration in the visible region for many years because of its persistency and few, if any, acute toxicological problems. Unfortunately, the properties that make fog oil an optimal obscurant (low vapor pressure) make it worthless as a fuel for vehicle engines. To reduce the logistics burden, it is desirable to use a common material for smoke generation and for fuel to operate armored vehicles and other equipment. The Army has selected JP-8, a jet fuel, as the one fuel forward in combat arenas. Unfortunately, JP-8 is too volatile to produce effective smoke - especially in warm weather.¹

The production of effective obscurants from volatile liquids has proved to be one of the major developmental challenges. Liquid aerosol smoke is usually generated on the battlefield by the vaporization/condensation method. The liquid is vaporized by heating before the gas is disseminated into the atmosphere. Upon cooling, it condenses into a liquid aerosol with a particle size about 1 micron. Because JP-8 is quite volatile, it fails to condense or condenses initially and then revaporizes into a gas. If a procedure could be developed to convert its components into analogous compounds having lower vapor pressures, then JP-8 could be used as the feed stock for a useful obscurant. This development would thereby permit the use of a single fuel for both smoke production and engine operation.

2. BACKGROUND

2.1 Meetings and Identification of Problem.

Attempts to reduce the volatility of fuel to improve obscuration have been proceeding for almost a decade. In June 1985, the Vice Chief of Staff of the Army directed that fog oil be replaced with diesel fuel by October 1986. In response, a meeting was held at the University of Florida in October 1985 to discuss possible approaches for meeting the directive. The suggestions could be divided into 3 categories -- (1) chemical modification of the hydrocarbons into less volatile analogs, (2) addition of surfactants to reduce evaporation, and (3) thermomechanical methods for smoke generation.²

Before fog oil could be replaced by diesel fuel, the decision was reached to use JP-8 in all tactical vehicles to phase out diesel fuel and gasoline. A consequence of this decision is the need now to generate smoke from JP-8, a fuel more volatile than diesel fuel. The problem was clearly demonstrated at Dugway Proving Ground. The Vehicle Engine Exhaust System (VEESS) generated adequate smoke with Diesel DF-2; whereas, JP-8 was unacceptable. To meet this challenge, a Short Term Analytical Study (STAS) panel

convened at the U.S. Army Chemical Research, Development and Engineering Center (CRDEC) now known as the U.S. Army Edgewood, Research, Development and Engineering Center (ERDEC) in May and July 1989 to discuss the problem and propose possible solutions. The panel concluded that thermomechanical approaches such as altering the feed rate and/or modifying the exhaust plume would be relatively easy to effect but would probably provide only marginal improvement. Substantial modifications to the VEES itself or changes in the properties of the fuel were more promising but would require more time and a considerably greater effort.³

Table 1 summarizes relevant properties for JP-8, Diesel Fuel #2, fog oil, two synthetic lubricants, Emery 3002 and Emery 3004 (prepared by polymerizing 1-decene), and PEG 200, a condensation polymer of ethylene glycol.

Table 1. Physical Properties of Liquid Smoke Materials

Property	JP-8 ³	Diesel Fuel ⁴ #2	Emery ⁵ 3002	Fog Oil ⁴	Emery ⁵ 3004	PEG ⁴ 200
Mean Molecular Weight	170	201	287	300	437	201
Boiling Point (°C)	200	265	310	370	402	310
Distillation End Point (°C)	300	343	310	465	--	--
Heat of Vaporization (btu/pound)	--	104	--	92	--	170
Flash Point (°C)	45	--	155	--	215	--
Viscosity @ 40°C (cSt)	--	2.9	5.5	22.5	16.8	24
Specific gravity	0.80	0.85	0.80	0.92	0.82	1.27

2.2 Previous Attempts to Modify Fuels.

There have been several attempts to produce a less volatile material from diesel fuel, kerosene, and/or jet fuel. The following paragraphs summarize some of the previous research.

Platz *et al*⁶ attempted a catalytic polymerization using a two-step process involving first dehydrogenation of the hydrocarbons followed by polymerization of the resulting olefin. The goal of this approach was to increase (double) the molecular weight of the volatile components - thereby reducing their vapor pressure. In step 1, several dehydrogenation catalysts were tested -- platinum on alumina, platinum on carbon, nickel on alumina, and platinum on zeolite. The yield of olefins increased with increasing temperature reaching a maximum (11%) at 600 degrees C with a CoMoS₂ catalyst. The investigators chose an SK-500 zeolite catalyst for the polymerization reaction. The catalyst was very effective at 250 ° C in promoting the alkylation of many of the components of diesel fuel when octadiene or styrene were added to the reaction. Unfortunately, the two-stage system working as a unit was not effective in substantially increasing the molecular weight of the hydrocarbon mixture - presumably due to difficulties in dehydrogenating the initial diesel fuel.

Eugene Song⁷ at CRDEC attempted a liquid phase oxidation of diesel fuel by bubbling air through a fuel mixture at elevated temperatures (100-160 ° C) and pressures (100-200 psi) at a rate of 0.75 l/min for about 2 hr. Among the catalyst tried, cobalt carboxylate was superior to cerium carboxylate, manganese carboxylate, cobalt acetylacetonate, and manganic acetylacetonate. The process generated significant quantities of carboxylic acids during the 2-hr reaction; however, the liquid phase oxidation system was too slow for field use. Nevertheless, the concept of generating new compounds with lower vapor pressure was demonstrated.

Clausen *et al*,^{8,9} attempted to eliminate the volatility problem entirely by converting diesel fuel into carbon particles by incomplete combustion. Carbon particulate yields of about 40% could be achieved with an air/fuel ratio of about 6:1. The carbon/diesel fuel mixture was superior in obscuration in both the visible and infrared (IR) regions to liquid aerosol smokes produced by vaporization/condensation of diesel fuel.

Porter and Besenbruch¹⁰ attempted to reduce the vapor pressure of diesel fuel by adding surfactants. They observed a significant reduction in the vapor pressure of decane upon addition of F(CF₂)₁₂(CH₂)₁₂H. Addition of the fluorohydrocarbon certainly decreased the rate of vaporization (as does any material that forms a solution) of the liquid, but no explanation was given about how the process could improve the condensation of the vapor or retard revaporization of the aerosol.

Clausen *et al*¹¹ also attempted to improve the obscuration properties by reacting diesel fuel with ozone (O₃) at ambient temperature. Based on changes in the infrared spectrum

(i.e., addition of C=O stretch at 1700 cm⁻¹) and increase in the neutralization equivalent, Clausen and co-workers concluded that carboxylic acids had been produced by an ozonation reaction. The yield was about 10 % in the aerosol fraction and 15-20 % in the residue in the evaporation tube. Unfortunately, the persistency of the modified or oxidized fuel was about the same as the initial diesel fuel.

Solash¹² attempted to convert diesel fuel to a more effective smoke material by three different methods. The first was a modification of a Friedel Crafts reaction in which the diesel fuel was heated with various Lewis acids, SnCl₄, TiCl₄, and AlCl₃. Normally the Lewis acid catalyses the formation of a nucleophilic species from an alkyl halide or an olefin that subsequently reacts with an aromatic compound. This is an example of the classic reactions in organic chemistry for producing substituted aromatics. The hope was that heating the diesel fuel with the catalyst would lead to some type of cracking process that would generate the requisite nucleophilic. The procedure led to a material with a slight increase (5%) in viscosity and perhaps a higher boiling point. Addition of an olefin (1,7-octadiene) to the reaction did lead to a higher boiling material.

The second approach was liquid phase oxidation of the hydrocarbon with the following catalysts: cupric acetate, manganese dioxide, cobalt chloride, cupric chloride, and cuprous oxide. After bubbling air through the system, they observed an increase of about 20% in the boiling point of the lighter fractions. Little change was observed in the higher boiling fractions.

The third approach was an ultrasonic alkylation based on a patent by Huges and Veatch¹³ in which a refluxing diesel fuel was subjected to 50-150 watts of 20 kHz ultrasound. This procedure apparently had no effect on the hydrocarbons.

Following the Diesel Fuel Conference,² Sliepcevich conducted some experiments based on thermomechanical approaches.¹⁴ Rather than alter the composition of the liquid feed, he attempted to alter some of the generator parameters. He observed a significant improvement in smoke from diesel fuel when the outlet temperature was reduced from 900 °F (482 °C) to 700 °F (371 °C). There was some improvement when water (to promote nucleation) was added to the diesel fuel prior to vaporization. The addition of salts either mixed with the diesel fuel prior to vaporization or added later to the vaporized gases had no significant impact.

3. THEORETICAL EVALUATION

3.1 JP-8 Composition.

JP-8 is a mixture of hydrocarbons distilling in the range from 155 to 260 °C with a median boiling point approximately 200 °C. The exact composition varies, depending on the source of the crude.¹⁵ JP-8 derived from petroleum consists principally of straight chain hydrocarbons C₁₁ through C₁₄ in approximately equal concentrations with smaller

amounts of C₁₀ and C₁₅. Minor components include hydrocarbons of higher and lower molecular weight, branched chain and cyclic hydrocarbons, substituted aromatics and polynuclear aromatics. In contrast, the JP-8 prepared from coal contains considerably higher quantities of aromatic compounds. The structures of selected JP-8 components and other compounds studied in this project are delineated in Table 2.

Table 2. Chemical Structures

n-OCTANE	CH ₃ -(CH ₂) ₆ -CH ₃
n-DECANE	CH ₃ -(CH ₂) ₈ -CH ₃
n-TETRADECANE	CH ₃ -(CH ₂) ₁₂ -CH ₃
DECANOL	CH ₃ -(CH ₂) ₈ -CH ₂ -OH
DODECANOL (LAURYL ALCOHOL)	CH ₃ -(CH ₂) ₁₀ -CH ₂ -OH
TETRADECANOL (MYRISTYL ALCOHOL)	CH ₃ -(CH ₂) ₁₂ -CH ₂ -OH
3-TETRADECANOL	CH ₃ -CH ₂ -CH(OH)-(CH ₂) ₁₀ -CH ₃
ETHYLENE GLYCOL	HO-CH ₂ -CH ₂ -OH
PROPYLENE GLYCOL (1,2 PROPANEDIOL) (1,2 DIHYDROXYPROPANE)	HO-CH ₂ -CH(OH)-CH ₃
1,10 DECANEDIOL	HO-(CH ₂) ₁₀ -OH
PEG 200 (POLYETHYLENE GLYCOL)	HO-(CH ₂ -CH ₂ -O) ₃ -CH ₂ -CH ₂ -OH (PRINCIPALLY)
EMERY 3002	CH ₃ -(CH ₂) ₉ -CH ₂ (CH ₃)-(CH ₂) ₇ -CH ₃ i.e. [\bullet CH ₂ -CH ₂ -(CH ₂) ₇ -CH ₃] ₂ (PRINCIPALLY)

Table 2. Chemical Structures (Continued)

EMERY 3004	75% [$\bullet\text{CH}_2\text{-CH}_2\text{-(CH}_2)_7\text{-CH}_3$] ₃ 25% [$\bullet\text{CH}_2\text{-CH}_2\text{-(CH}_2)_7\text{-CH}_3$] ₄
3- PENTANONE (DIETHYL KETONE)	$\text{CH}_3\text{-CH}_2\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-CH}_2\text{-CH}_3$
3-DECANONE	$\text{CH}_3\text{-CH}_2\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-(CH}_2)_6\text{-CH}_3$
8-TETRADECANONE	$\text{CH}_3\text{-(CH}_2)_6\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-(CH}_2)_5\text{-CH}_3$
DECYL ALDEHYDE (DECANAL)	$\text{CH}_3\text{-(CH}_2)_8\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-H}$
TRIDECYL ALDEHYDE	$\text{CH}_3\text{-(CH}_2)_{11}\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-H}$
DODECANOIC ACID (LAURIC ACID)	$\text{CH}_3\text{-(CH}_2)_{10}\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-O-H}$
TETRADECANOIC ACID (MYRISTIC ACID)	$\text{CH}_3\text{-(CH}_2)_{12}\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-O-H}$
HEXADECANOIC ACID (PALMITIC ACID)	$\text{CH}_3\text{-(CH}_2)_{14}\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-O-H}$
OCTADECANOIC ACID (STERIC ACID)	$\text{CH}_3\text{-(CH}_2)_{16}\text{-}\overset{\text{O}}{\underset{\parallel}{\text{C}}}\text{-O-H}$
ROSCO FOG FLUID	30 % WATER 30 % TRIETHYLENE GLYCOL 20 % 1,2-PROPYLENE GLYCOL 20% 1,3-BUTANEDIOL

To be successful, a system must be developed that will reduce the volatility of the C₁₁ and C₁₂ components substantially and reduce the C₁₃ and C₁₄ components moderately.

Components above C₁₄ should produce adequate smoke without extensive modification. It would be beneficial if the C₁₀ and lower components could be converted to useful compounds; however, because they are present in low concentration, effect on smoke yield and persistency will be minimal.

3.2 Research Approach for Reducing Volatility of Hydrocarbons.

Previous research has demonstrated the oxidation of hydrocarbons to carboxylic acids and other species. Unfortunately, the yield was too low or the reaction too slow to be militarily useful. The principal reason for the lack of success was the low concentration of oxygen in the liquid phase relative to the concentration of hydrocarbons. A gas phase system would allow introduction of sufficient oxygen (as air) to increase the rate of oxidation. The gas phase would also facilitate material transfer with the heterogeneous catalyst.

A major objective of this project was to determine the point at which alcohols and other compounds are too volatile to produce satisfactory smoke. Compounds with high volatility must be oxidized more (additional oxygen atoms added) than less volatile compounds to produce persistent aerosols. Information from this study will be used to determine the oxidation end points. That is, the catalyst (or catalysts) and the operating parameters will be selected that produce a high yield of highly oxygenated compounds from the lighter components but do not generate tar that may clog the system from the less volatile components.

The volatility of materials is directly related to the vapor pressure. Comparison of the boiling points (i.e., the temperature at which the vapor pressure equals the atmospheric pressure) for different liquids provides a relative or approximate ranking of their volatility. Boiling point data is available for more compounds than vapor pressure data and therefore with certain restrictions will be the basis for comparing different compounds. The heat of vaporization is the energy that must be added to a liquid to overcome the intermolecular forces and thereby allow the molecule to escape into the vapor phase. The vapor pressure at any temperature can be calculated exactly with the Clausius-Clapeyron equation if (1) the vapor pressure at one temperature and (2) the heat of vaporization as a function of temperature are known.

$$\frac{dp}{dt} = \frac{P \Delta H}{RT^2}$$

The equation indicates that the change in vapor pressure as a function of temperature will be greater for compounds with a higher heat of vaporization. At temperatures below their boiling points, compounds with considerable intermolecular hydrogen bonding like alcohols and carboxylic acids have a lower vapor pressure than hydrocarbons having the same boiling point. Therefore, aerosols composed of alcohols, etc., will be more persistent than would be expected from boiling point data alone. The greater heat of vaporization that must come from the surrounding atmosphere results in the formation of

less vapor. Initially, the heat of vaporization will hamper the formation of an aerosol because the heat must be transferred from the system; however, this has not normally been as great a problem for smoke systems as the subsequent evaporation of the aerosol. Also, many of the alcohols and carboxylic acids are solids at ambient temperature. If they are able to cool sufficiently to crystallize, then evaporation requires the additional heat of fusion (melting).

The plan is a vapor phase oxidation of the straight chain hydrocarbons and other components to alcohols, carboxylic acids, diols, and possibly other compounds that have a lower vapor pressure than the corresponding hydrocarbons. The engineering concept is to pass the vapor and air (i.e., oxygen) through a tube or pipe containing a solid phase catalyst - probably some transition metal. The catalyst needs to be efficient (rapid oxidation) but it does not have to be highly selective. For example, dodecane could be oxidized to a mixture of 1-dodecanol, 2-dodecanol, 3-dodecanol, 1,12-dihydroxy-dodecane, 1,2-dihydroxydodecane, lauric acid, and numerous other compounds. The only requirement is that the catalyst not degrade the hydrocarbon chain and form carbon dioxide or short chain species.

Figure 1 illustrates the increase in boiling point with increasing molecular weight for a series of straight chain hydrocarbons, n-alcohols, carboxylic acids, and α,ω diols. For comparison purposes, the boiling points and boiling ranges of fuels are included. *The long term objective of the project is to convert hydrocarbons boiling in the 175-250 °C range into analogs that boil in the 300-350 °C range.* The graph indicates an almost linear increase in boiling point with each C_2H_4 addition. The C_{12} hydrocarbon is too volatile for obscuration in hot weather. Oxidation of a terminal carbon to a hydroxyl increases the boiling point from 216 °C to 257 °C -- approximately the mean for diesel fuel. Further oxidation at the same carbon generates the analogous carboxylic acid with a boiling point around 300 °C. Another reaction path in which the carbon at the distal carbon is oxidized to another hydroxyl produces the α,ω diol with a boiling point of 320 °C. A similar procedure would increase the boiling point of the C_8 components (octanol), which are too volatile to persist except in the coolest conditions, from 126 °C to 230-270 °C range.

Aldehydes and ketones are other possible products that could be obtained by oxidation of the hydrocarbons or more likely from the corresponding alcohols. In general, the boiling points of aldehydes and ketones are 5-10 °C lower than the corresponding alcohols due to the reduction in intermolecular hydrogen bonding. Ketones are stable compounds, usually formed by the oxidation of secondary alcohols, that would be suitable for smoke generation. Aldehydes contain a carbonyl functional group similar to ketones but are formed by oxidation of primary alcohols. Because aldehydes are easily oxidized to carboxylic acids, they are somewhat difficult to prepare. Frequently, commercial grade aldehydes contain significant quantities of the corresponding carboxylic acid due to oxidation by air during preparation and/or storage. If any aldehyde was produced, it would most likely be further oxidized to the corresponding carboxylic acid by spontaneous

BOILING POINTS OF SMOKE CANDIDATES

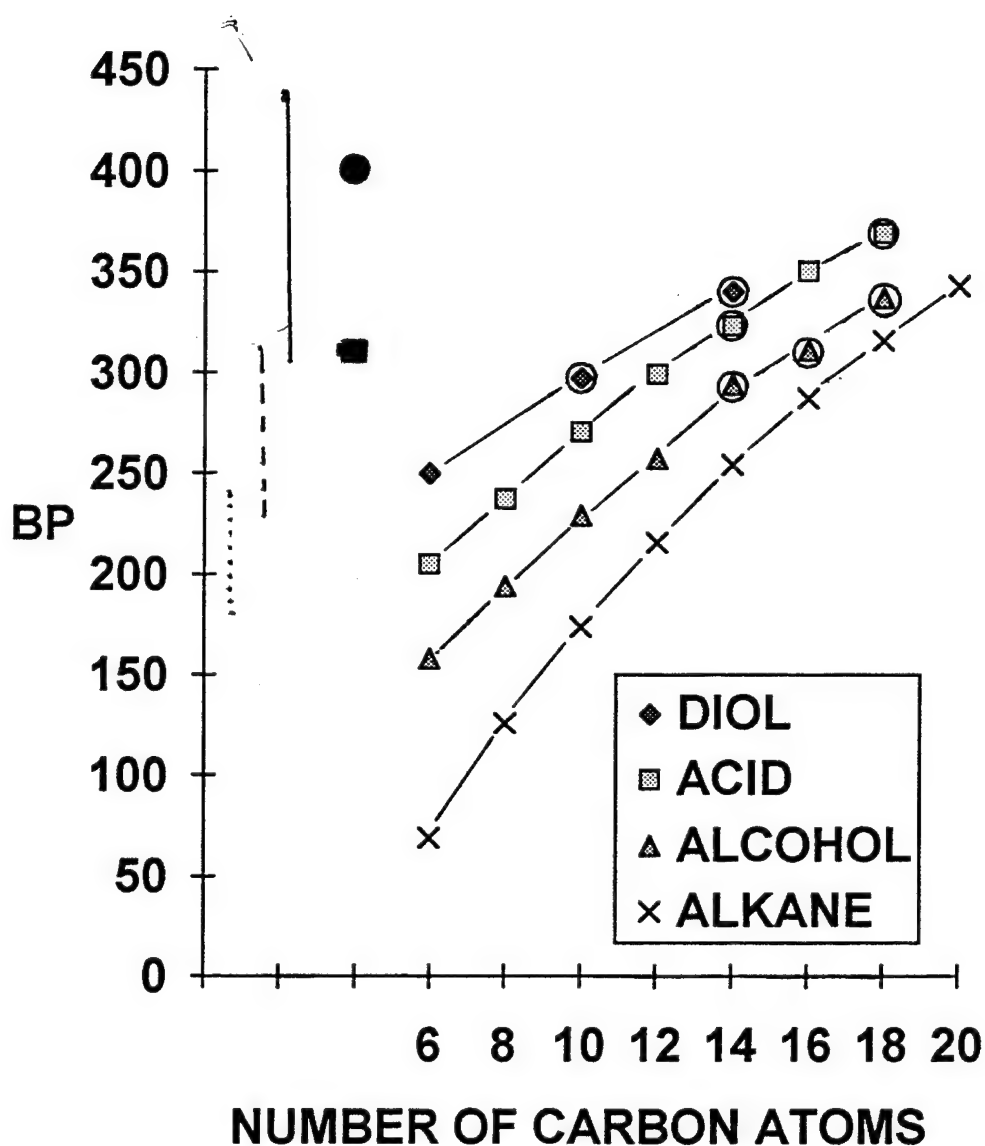


Figure 1. Boiling Points (°C) for a series of hydrocarbons (alkanes), primary alcohols, carboxylic acids, and α,ω diols. The principal boiling ranges (10-90%) are also indicated for JP-8 (dotted line), #2 diesel fuel (dashed line), and fog oil (solid line). The alpha olefins Emery 3002 and Emery 3004 are indicated by a solid square and solid circle, respectively. Symbols enclosed by open circles indicate values that were calculated by the Hass-Newton method. Other values were taken directly from the literature.

reaction with oxygen in the air or in the catalysis vessel itself. Thus, it seems unlikely that aldehydes would be a likely product of gas phase oxidation of hydrocarbons.

Boiling points for compounds in Figure 1 at one atmosphere were obtained directly from the literature¹⁶ or calculated using conventional techniques. The procedure of Hass and Newton,¹⁷ calculating boiling points from empirical data at reduced pressure, gave more accurate results than methods based on addition of component values. In the Hass-Newton equation

$$\Delta t = \frac{(273.1 + t)(2.8808 - \log p)}{\phi + .15(2.8808 - \log p)}$$

ϕ provides an estimate of the heat of vaporization at different temperatures and is equal to $\Delta H_{\text{vap}}/2.3RT_b$. The major difficulty in using the Hass-Newton equation is determining which group to use when selecting the value of ϕ . Fortunately, the normal boiling point and the boiling point at reduced pressure were known for a few compounds of interest. By calculating the boiling points with different values of ϕ and comparing the results to literature values, it was determined that group 5 gave the most accurate calculations. Therefore, group 5 values were used to calculate the other boiling points. Compounds were not included in the table when the boiling points were determined at pressures less than 5 mm because the long extrapolation produces an unacceptable error.

3.3 Objective of Smoke Generation Experiments.

The calculations above strongly suggest that dodecanol and other compounds equally or less volatile should produce adequate smoke. Before initiating a major effort to identify suitable catalysts to effect the required oxidations, it was important to verify that the products of the desired oxidation of JP-8 produce adequate smoke. *The purpose of the initial study described in this report was to delineate the boiling ranges for the expected products and to confirm that they produce a useful smoke by the vaporization/condensation method.* The efforts concentrated on the shorter components present in JP-8 because they are more likely than the longer components to produce ineffective smoke. If the more volatile components produce useful smoke, the less volatile will also. The experiments were designed to maximize field conditions and still provide a reproducible environment with which to compare the candidates with established smoke candidates.

3.4 Choices for Design of Smoke/Obscuration Experiments.

Experiments are designed to control or regulate specific variables and minimize the uncontrollable variables. This approach is most likely to generate reproducible data and results that can be compared with other experiments. A tightly controlled laboratory environment may be highly reproducible but usually does not reflect the field conditions. In contrast, an outside experiment may be so loosely ordered that no data can be collected -- only subjective observations made.

A smoke generation experiment conducted outdoors is identical to an operational situation; however, reproducing the meteorological conditions is usually impossible even when the time between successive runs is short. Slight changes in wind, impossible to detect without instruments, blow the smoke in different directions away from the sensors and accelerate the breakup of the cloud.

At the other extreme, a small chamber allows conditions to be reproduced exactly; however, the vapor may reach a saturated state quickly, and the aerosol may persist indefinitely until the liquid coalesces into larger droplets or deposits on the wall of the chamber. *Persistency studies whose objective is measuring rates of evaporation are meaningless in saturated conditions because no evaporation is possible.*

The breeze tunnel located in E-5884 has a large volume to permit reevaporation of the aerosol and a controlled wind velocity of 5 mph. The only limitation is the relatively short duration time in the chamber making persistency measurements impossible.

The fourth option is a large partially open chamber. This type of system is sufficiently large to permit evaporation of the volatile components but offers some protection from the wind - thereby permitting comparison of different materials. The static nature of the system permits measurements over extended periods and allows persistency estimates to be made. Because the system is not completely airtight, some varying air currents may blow the smoke in different directions and therefore change the aerosol concentration near the sensors. Therefore, different trials may not produce identical results.

4. EQUIPMENT

4.1 Chemicals.

All chemicals were obtained from commercial sources. Purity was greater than 98% as determined qualitatively using a GC/MS and quantitatively with GC using a thermal conductivity detector.

4.2 Aerosol Measurements.

The Real-Time Aerosol Sensor (RAS) is a particulate concentration monitor whose operation is based on the scattering of near infrared radiation. The sensor employs a GaAlAs light source with a narrow band emission centered at 880 nm. The radiation scattered by the aerosol is detected in a region 45-95 degrees from the forward direction. The scattering is monitored continuously as the particles pass through the sensing region (aprx 1 cm³.) Sampling results from the free passage of air through the chamber. No pump is used to move air pass the sensor.

Voltage output from the RASs was collected on a Dolch 386 portable computer using the Keithley EasyESTLX program. Data was recorded at 0.1-second intervals and stored on floppy disks prior to data reduction.

4.3 Aerosol Generation.

Smoke was generated in the shelter with a TDA 5A smoke generator manufactured by the TSI Corporation. The liquid was vaporized by passing it through or over a plate whose temperature is maintained at 750 °F (400 °C). Carrier gas was provided from a nitrogen cylinder attached to the gas inlet of the smoke generator. A ready light indicated that the heating block was in the correct operating temperature. Liquid was contained in a metal bottle within the apparatus. When the "aerosol" toggle switch was in the *on* position, air (or nitrogen) flows from the orifice. Opening the screw valve allowed liquid to enter the system and smoke begins to form in a few seconds.

Smoke was also produced with the Rosco Theatrical Fogger. This apparatus was designed to produce a smoke cloud for visual effects at concerts and other public events. Its operation is similar to the TDA 5A except it has a self-contained pump to force the liquid through the hot plate and therefore does not require a carrier gas source. Although no quantitative comparisons were made, it appears that the capacity of the TDA 5A is slightly greater than the Rosco - probably because the vaporization chamber operates at a higher temperature.

The Smoke Master is a portable smoke generator that resembles a shoulder fired weapon. Liquid is contained in a metal pressure bottle. Depressing a trigger on the instrument opens the valve on the pressure bottle and allows liquid to enter the quarter inch copper tubing (coiled around a propane burner) where it is vaporized as it passes through the heated coils before being discharged through the nozzle into the atmosphere.

For this study, the Smoke Master was clamped to a metal table in an inverted position to facilitate controlled addition of the liquid at low pressure. Liquid was fed from a glass bottle through tygon tubing to the copper tubing. Pressure was maintained at 2.5 psi with nitrogen from a cylinder. The Smoke Master did not generate sufficient heat to vaporize the liquid under the experimental conditions even with the torch at maximum. The liquid merely passed through the copper tubing and was discharged as a stream from the orifice. Some smoke was produced at the end of the run when the tube contained principally nitrogen and only a small amount of liquid. No data was collected with this apparatus.

4.4 Smoke Containment.

4.4.1 Small Chamber. A 1 m³ rectangular chamber constructed of Plexiglas contained sealed doors for access and a 2 inch circular hole for introducing the smoke. Three RASs were positioned inside on top of a platform 12 inches above the floor. RAS 1 was placed in the center about 18 inches from the aerosol outlet. RAS 2 and RAS 3 were located 8 inches to the left and right, respectively. All RASs were positioned on their side

so that the light beam was horizontal. This orientation minimized coating the windows as a result of aerosol settling or deposition.

4.4.2 Cloche. The principal smoke chamber used in this study was a Quonset hut or cloche constructed of polyethylene supported by a series of semicircular ribs having a 7 ft radius. The structure was 95 ft long. The generator was placed on a small table 40 inches high and located 10 ft inside the front entrance. The two RASs were suspended from the ceiling 5 ft from the ground - the first 10 ft downstream and the second 17 ft downstream. The front entrance was covered with polyethylene to provide a barrier to smoke escape; the rear entrance was open. This was the same structure used in previous studies for generating aerosols with the Noel-Penny turbine engine.¹⁸

Usually, the vapor would begin to condense about an inch from the nozzle. Occasionally, depending principally on the liquid, vaporization would be incomplete. This problem was immediately detected by the appearance of liquid coming from the nozzle, by a pulsating sound as the liquid passed through the nozzle, and by the ready light going off, indicating that the heating block had been cooled below the operating temperature.

5. EXPERIMENTAL PROCEDURES

5.1 Data Reduction.

According to the RAS Manual,¹⁹ the output voltage can be converted to concentration with the following formula:

$$\text{Conc (mg/m}^3\text{)} = 1/16 \times \text{output voltage (mV)}$$

Because different quantities of liquid were consumed during trials, the data was converted to milligrams of aerosol/cubic meter/gram of liquid consumed. This value was obtained by determining the mean voltage from the RASs, dividing by 16 to obtain the aerosol concentration, and dividing this quotient by the mass (grams) of material consumed. The mass consumed was the produce of the volume consumed and the density.

5.2 Chamber Procedures.

The Rosco Theatrical Fogger was positioned outside the 1 m³ with the nozzle opposite a 2 inch hole cut approximately in the center of the chamber wall. The test liquid was drawn from a glass bottle into the generator through tygon tubing. Prior to initiating a run, the Rosco was allowed to warm until the ready light came on, indicating the heating block was in the operating range. The data collection was begun and smoke was generated for 15 seconds. The amount of liquid consumed was too small to measure.

5.3 Cloche Procedures.

The test liquid was placed in the internal reservoir of the TDA 5A smoke generator. The apparatus was allowed to warm (approximately 20 min. when cold) until the light indicated the system was operational. A mark (actually tape) was placed on the transparent tubing to indicate the level of liquid. A small fan was placed on the ground about 3 ft in front of and 3 ft below the generator and positioned so the air movement was directed upward - 90 degrees from the direction of initial smoke stream. The purpose of the fan was to increase the mixing of the smoke with surrounding air and thereby minimize aerosol gradients; however, the fan did not appear to have any significant impact. At $T = 0$ min, the base line data collection began. At $T = 2$ min, smoke generation began by moving the smoke generation toggle switch to the *on* position and opening the valve, thereby allowing the test liquid to flow from the reservoir into the hot chamber. Nitrogen entering the TDA 5A was maintained at 2.5 psi. At $T = 5$ min (3 min of smoke generation), the reservoir valve was closed and after smoke generation ceased (about 15 seconds), the toggle switch moved to the *off* position. Data was normally collected for another 15 min. At the end of the test, the reservoir was filled to the initial mark to determine the volume of liquid consumed.

6. RESULTS

Figure 2 illustrates the results of the initial study in the chamber. The purpose of the initial trial was to test the smoke generation equipment and monitor the reproducibility and range of the Real-Time Aerosol Sensors (RAS). The concentration at the three sensors reached a maximum soon after the smoke generation was completed and slowly decreased. Because the volume inside the chamber was small, a saturated condition was quickly achieved. Therefore, smoke could only dissipate by sorption on the walls of the chamber or through small leaks in the system. In this system, ethylene glycol, decanol, and the Rosco Fog Fluid produced comparable smokes. Propylene glycol was totally ineffective as previously reported.²⁰ Because this small chamber was not appropriate for the qualitative evaluation of the smoke characteristics, the remaining experiments were conducted in the cloche.

The design of the cloche permitted testing of smoke generation and persistency over a range of temperatures. Early in the morning, the temperature was usually around 70 °F (21 °C). In the afternoon, especially on sunny days, the temperature would rise to 105 °F (40 °C).

Dodecanol produced high quality smoke. Upon generation (depending upon wind direction), the cloud slowly moved forward toward the rear end of the shelter or blew back toward the front. Traces of white smoke normally escaped through small holes in the plastic. Figure 3 illustrates the limitations of the cloche system in yielding reproducible data. Dodecanol was run at different times at ambient temperatures. In each

ONE METER CHAMBER

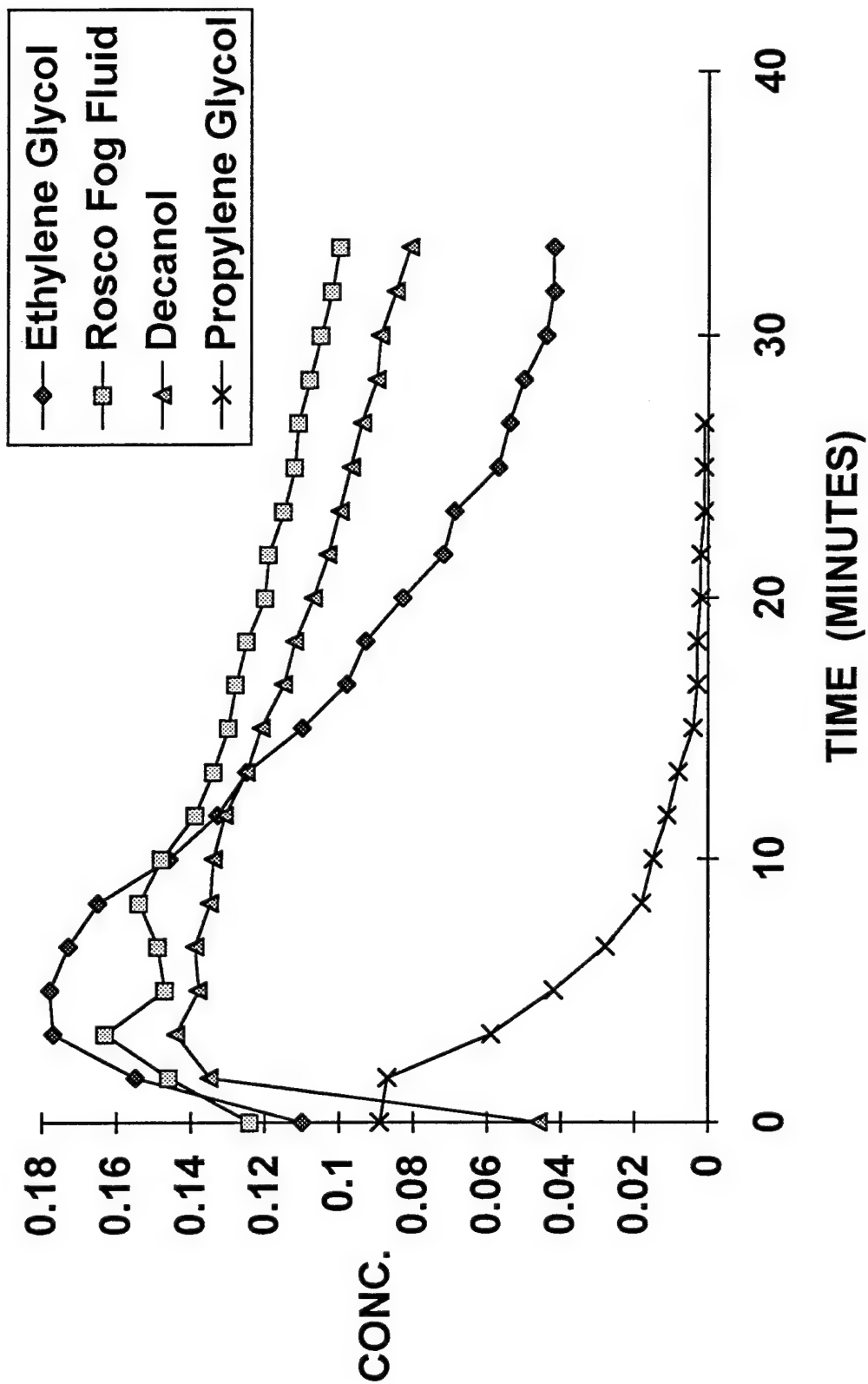


Figure 2. Persistence of Smoke in the 1 m³ chamber. Aerosol concentration is expressed as mg/m³/g of liquid consumed. Data for the graph are tabulated in Appendices A1-A4.

DODECANOL AT AMBIENT TEMPERATURE

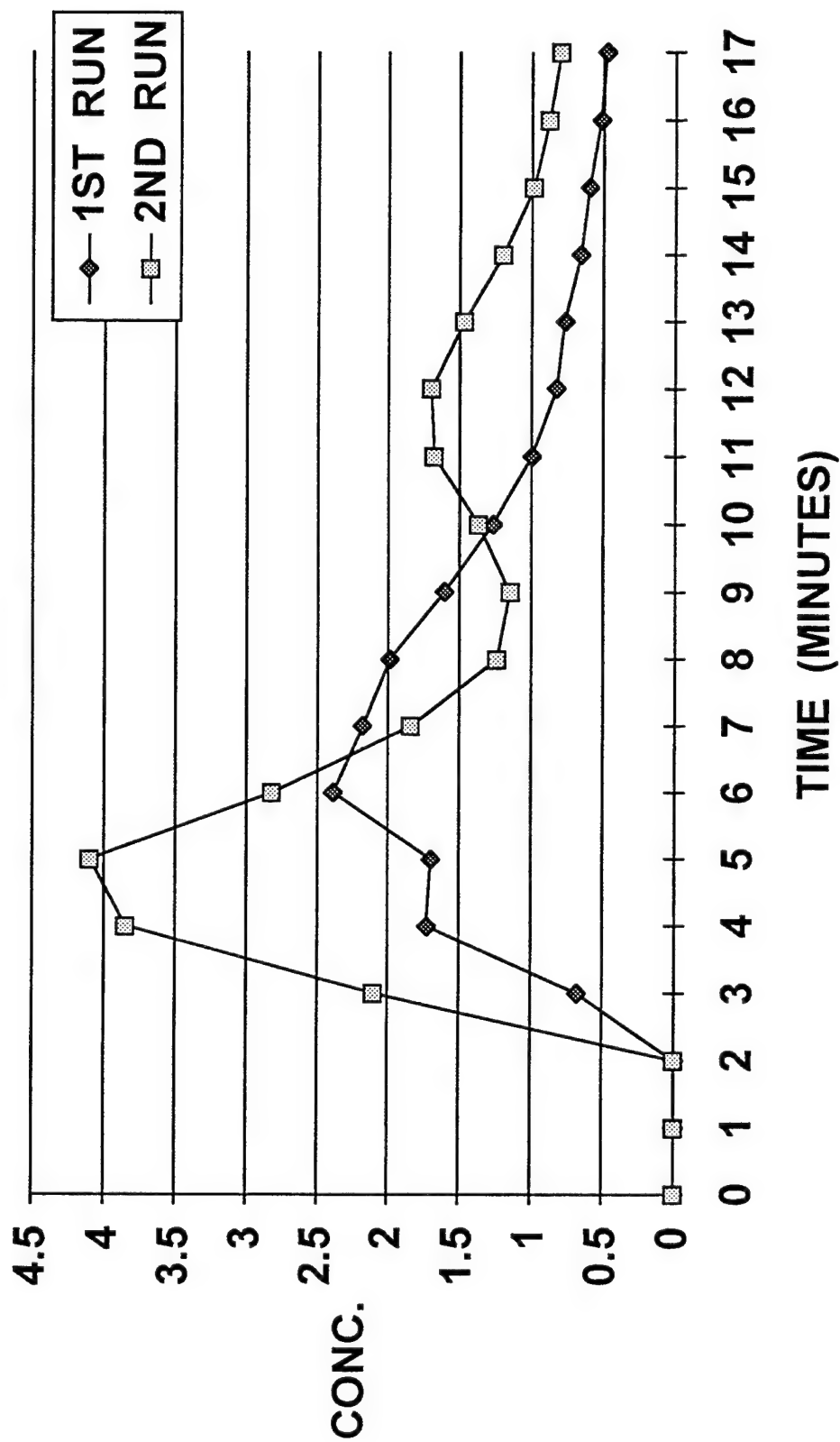


Figure 3. Persistency of dodecanol in the cloche at ambient temperatures. The 1st run was at 24 °C. The 2nd run was at 21 °C. Aerosol concentration is expressed as mg/m³/g of liquid consumed. Data for the graph are tabulated in Appendices A5 and A6.

experiment, the maximal concentration in the sensors was obtained near the end of the generation period. Then, the smoke slowly decreased during the next 15 min. Due to changes in wind direction, there was considerable variation in the aerosol concentration even with more than one sensor. The quantity of liquid consumed also varied for unknown reasons. To normalize the data and permit comparison of different materials, data was plotted as the concentration of aerosol per cubic meter per gram of liquid consumed. The large differences in aerosol concentration resulted from slightly different wind conditions that concentrated the aerosol around the sensor during the second run rather than permitting it to disseminate evenly. The second peak in the second run was due to a slight wind shift that blew the smoke back toward the sensors. Based on visual observations of the entire smoke generation and dissemination process, both runs were very similar.

As predicted from comparisons of vapor pressure and boiling points, Emery 3004 was the most persistent smoke material tested. At ambient temperatures, the smoke filled the entire cloche within 5 min and escaped at the rear opening. Emery 3002 was qualitatively almost as effective as 3004 at 25 °C; however, the smoke concentrated along the top of the cloche. Emery 3004 also showed this tendency, but it was much less (little smoke a foot above the ground) dramatic than Emery 3002. In contrast, the dodecanol smoke had no vertical separation. It is not known whether this phenomena is real (the density of the hydrocarbons and dodecanol is about the same but the heat of vaporization is lower) or an experimental artifact due to subtle differences in meteorological conditions. The dodecanol smoke was so dense that visibility was less than 2 ft. Figure 4 compares the aerosol concentrations of three different materials. The numerical values for Emery 3002 are artificially low because the sensors were not in the center of the cloud.

At temperatures above 100 °F (38 °C), the persistency of all smokes decreased considerably. These results are illustrated in Figure 5. The maximal value during the 3 runs with dodecanol (1.5 mg/m³/g of liquid) was only half that attained at ambient temperatures. Also, the smoke evaporated and/or dispersed faster with the sensors returning to background after about 10 min. The persistence of Emery 3004 was slightly longer. The maximal value for the single run was only 0.7 (compared to 2.0 at ambient); however, traces of the cloud could be detected after 20 min.

Both octanol and decanol generated smoke. The octanol cloud formed and concentrated around the two sensors. It did disseminate through the entire chamber but only formed a slight haze rather than an effective smoke. In contrast, the decanol cloud produced a useful smoke in the chamber; however, persistency was less than dodecanol. Figure 6 compares dodecanol with the shorter alcohols - octanol and decanol. All three are qualitatively similar - reaching a peak soon after the end of smoke generation followed by slow dissipation. As expected, the maximal concentration of the decanol aerosol is less than for dodecanol; however, it produces a marginal smoke in the 20-25 °C range. In contrast, octanol is probably too volatile to be of any obscuration value except at low temperatures. The maximum concentration for a run at 17 °C was about half that of decanol at 25 °C.

HIGHER MOLECULAR WEIGHT

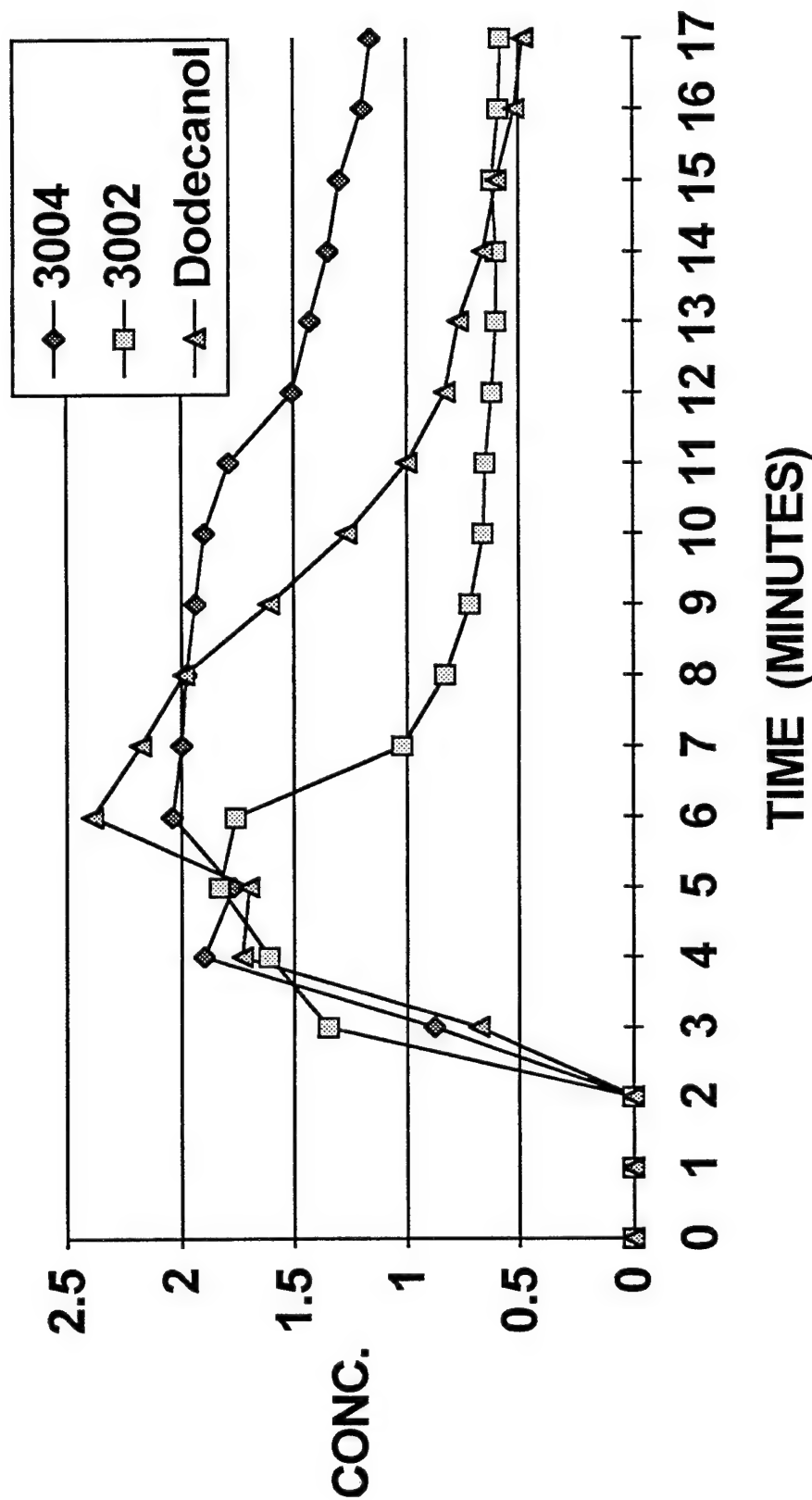


Figure 4. Comparison of the persistency in the cloche of dodecanol with two poly alpha olefins, Emery 3002 and Emery 3004. Dodecanol was run at 24 °C. Emery 3002 was run at 27 °C, and Emery 3004 at 24 °C. Aerosol concentration is expressed as mg/m³/g of liquid consumed. Data for this graph are tabulated in Appendices A5, A7 and A8.

HIGH TEMPERATURE

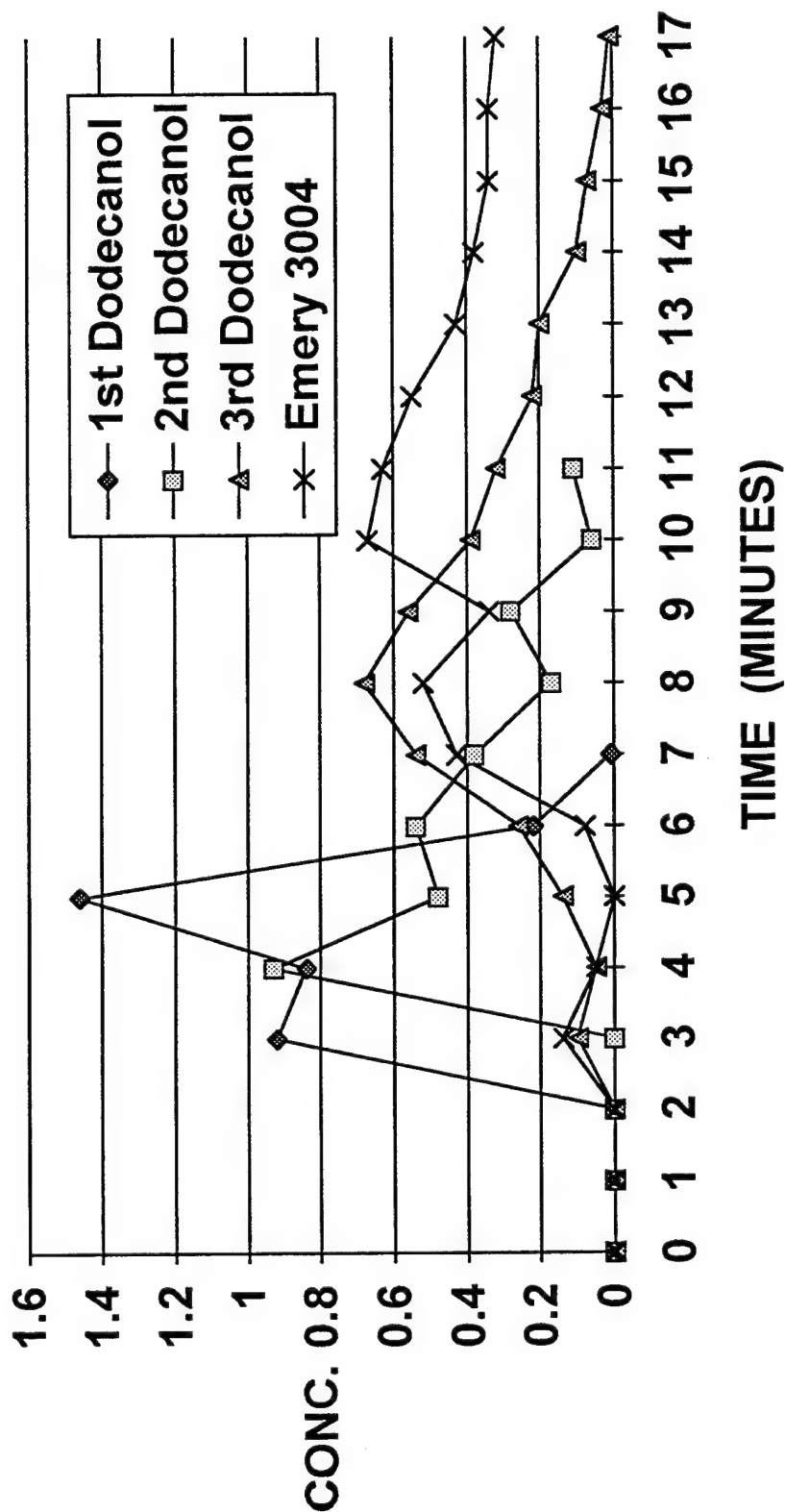


Figure 5. Persistency of dodecanol and Emery 3004 at higher temperatures. Aerosol concentration is expressed as $\text{mg}/\text{m}^3/\text{g}$ of liquid consumed. Run 1 was at 39°C ; run 2 at 39°C ; run 3 at 41°C and Emery 3004 at 36°C . Data for this graph are tabulated in Appendices A9, A10, A11, and A12.

LOWER MOLECULAR WEIGHT

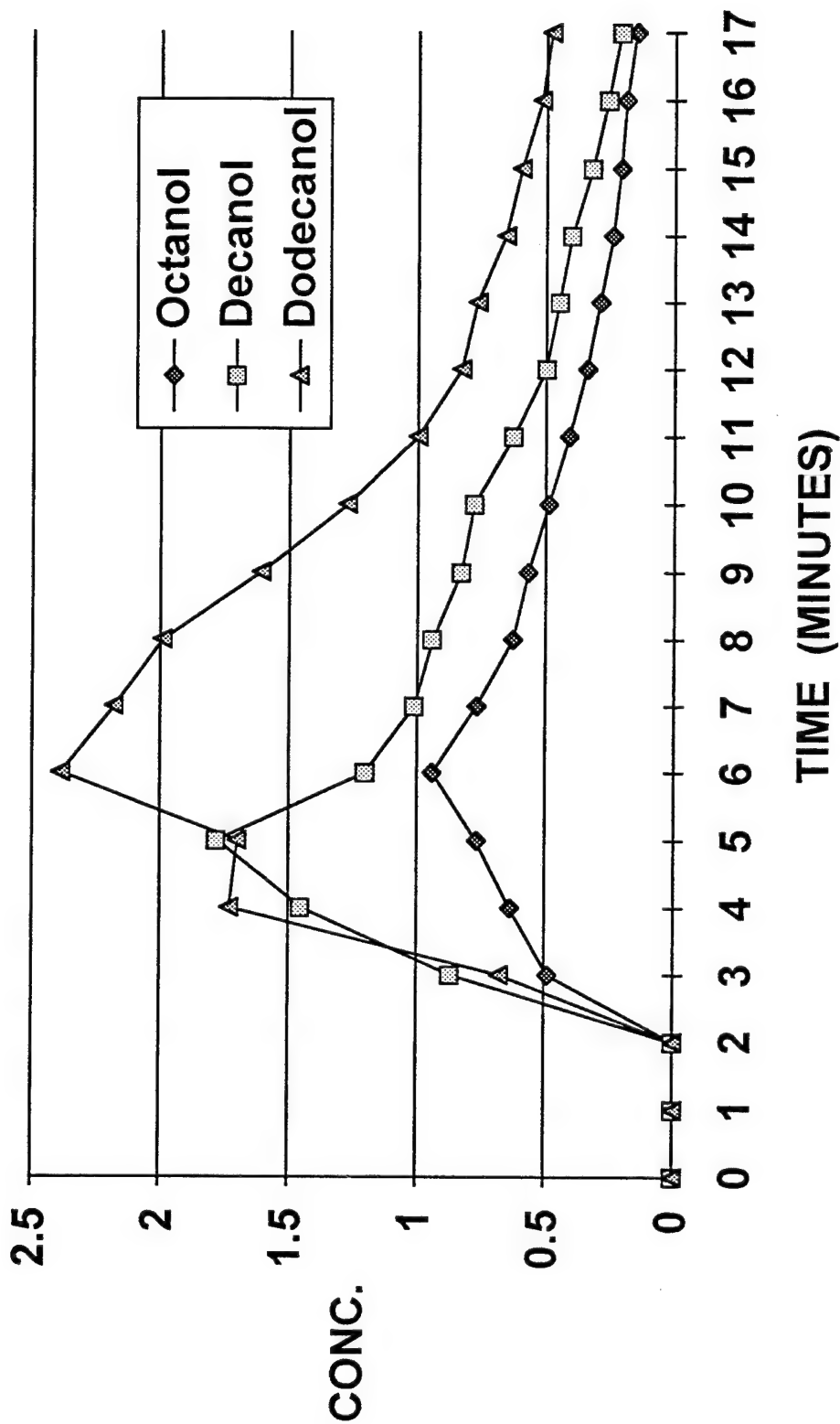


Figure 6. Comparison of the persistency in the cloche of lower molecular weight alcohols. Octanol was run at 17 °C, decanol at 26 °C, and dodecanol at 24 °C. Aerosol concentration is expressed as mg/m³/g of liquid consumed. Data for this graph are tabulated in Appendices A5, A13, and A14.

7. CONCLUSIONS

The long chain alcohols produce a useful smoke that persists for reasonable time. Dodecanol (C_{12}) is useful when temperatures are below 100 °F (38 °C) but evaporates rapidly at higher temperatures. Alcohols with longer hydrocarbon chains have lower vapor pressures and therefore should be more persistent. Decanol (C_{10}) is useful around 75 °F; whereas octanol (C_8) is only useful at cooler temperatures. JP-8 consists principally of hydrocarbons in the C_{11} to C_{14} range. Oxidation of dodecane (C_{12}), tridecane (C_{13}), and tetradecane (C_{14}) to alcohols will convert those components of JP-8 into useful smoke components. In contrast, it will be necessary to oxidize decane (C_{10}) and undecane (C_{11}) to carboxylic acids or diols to produce useful smoke materials. Even though oxidation of the C_{12} , C_{13} , and C_{14} components to corresponding alcohols will produce effective smoke constituents, further oxidation will generate a more effective smoke.

Emery 3004, a material already approved for use as an aerosol in filter testing, is a very effective smoke and could serve as a replacement for fog oil - especially in training situations. Emery 3002 would also be useful at cooler temperatures or in situations in which less persistency is desired.

BLANK

LITERATURE CITED

1. Clausen, Christian A.; Morgan, Paul W.; Leonard, Russell; and Slattery, James; *A Comparison of JP-8 Aerosols to Diesel Fuel and Fog Oil Aerosols*, CRDEC-CR-88031, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, January 1988, UNCLASSIFIED Report (ADB118 400L).
2. Rubel, Glenn O.; *Proceedings of the First Diesel Fuel Chemical Conference*, CRDEC-SP-87012, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report (ADB114 029L).
3. Rubel, Glenn O.; *STAS Panel Review of the JP-8/VEESS Smoke Issue*, CRDEC-TR-195, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1990, UNCLASSIFIED Report (ADB145 870L).
4. Rubel, Glenn O.; *Physical Constants of Standard Military Smokes*, ARCSL-TR-83025, U.S. Army Chemical Systems Laboratory, Aberdeen Proving Ground, MD, June 1983, UNCLASSIFIED Report (ADB077 591L).
5. Carlon, Hugh R. and Guelta, Mark A.; *Implementation of DOP Replacement with Selected Materials in Mask and Filter Testing Penetrometer Machines: Final Report*, CRDEC-TR-370, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1992, UNCLASSIFIED Report (ADA 254 560).
6. Platz, R.M.; McCarty, J.G.; Witham, C.L.; Kingsley, B.; Tong, G.T.; and Wood, B.J.; *Catalytic Polymerization of Diesel Fuel*, CRDEC-CR-87041, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, January 1987, UNCLASSIFIED Report (ADA176 908).
7. Song, Eugene; *Liquid-Phase Oxidation of Diesel Fuel*, CRDEC-TR-88136, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, August 1988, UNCLASSIFIED Report (ADB127 072L).
8. Clausen, Christian A.; Leonard, Russell; Movassaghi, Shahnaz; Slattery, James; and Williams, Robert; *Diesel Fuel Particle/Droplet Smokes*, CRDEC-CR-88037, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, February 1988, UNCLASSIFIED Report (ADB119 997L).

9. Clausen, Christian A.; Morgan, Paul W.; Leonard, Russell; and Slattery, James; *Carbon Particle Generation Studies*, CRDEC-CR-88049, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, March 1988, UNCLASSIFIED Report (ADB121 721L).

10. Porter II, John T. and Besenbruch, Gottfried E.; *Substitution of Fog Oil With Diesel Fuel Using Surfactant Technology*, CRDEC-CR-87082, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1987, UNCLASSIFIED Report (ADB113 592).

11. Clausen, Christian A.; Tronson, Soodabeh K.; Movassaghi, Shahnaz; and Williams, Robert A.; *Diesel Fuel Smoke*, CRDEC-CR-87042, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, January 1987, UNCLASSIFIED Report (ADB109 658L).

12. Solash, Jeffrey; *Substitution of Fog Oil with Diesel Fuel Using Liquid Phase Alkylation*, CRDEC-CR-87068, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, April 1987 UNCLASSIFIED Report (ADB111 534L).

13. Huges, Everett C.; and Veatch, Franklin; "Ultrasonic Alkylation," U.S. Patent 2,800,444, July 23, 1957.

14. Sliepcevich, C.M.; O'Rear, E.A.; and Lott, J.L.; *Substitution of Fog Oil with Diesel Fuel Using a Thermomechanical Approach*, CRDEC-CR-87009, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, November, 1986, UNCLASSIFIED Report (ADA175 357).

15. Song, Chunshan; Eser, Semih; Schobert, Harold H.; and Hatcher, Patrick G.; "Pyrolytic Degradation Studies of a Coal-Derived and a Petroleum-Derived Aviation Jet Fuel", *Energy & Fuels*, Vol 7, No. 2 (1993).

16. *CRC Handbook of Chemistry and Physics*, 74th. ed., Lide, David R., editor, CRC Press, Boca Raton, FL, 1993.

17. Hass, H.B. and Newton, R.F.; "Correction of Boiling Points to Standard Pressure" in *CRC Handbook of Chemistry and Physics*, 74th. ed, section 15 pp16-17, Lide, David R., editor, CRC Press, Boca Raton, FL, 1993, .

18. Guelta, Mark A.; Carlon, Hugh R.; Jolliffe, Robert V.; Paterno, Dorothea A.; Richardson, Theresa; and Grieb, Ronald S.; *Jet Engine Dissemination of Microcapsule Aerosols: An Experimental Study*, ERDEC-TR-061, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, May 1993, UNCLASSIFIED Report (ADB175 166).

19. *Real-Time Aerosol Sensor Model RAS-2 Operations Manual*, Monitoring Instruments for the Environment, Inc.; Billerica, MA, September 1990.

20. Vervier, Joseph J., and Anderson, David H.; *Laboratory Study of Vaporization/Condensation Smoke Materials*, ARCSL-TR-79037, U.S. Army Chemical System Laboratory, Aberdeen Proving Ground, MD, May 1979, UNCLASSIFIED Report (ADB038 262).

Blank

APPENDIX A1

ETHYLENE GLYCOL IN 1 M³ CHAMBER

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS 3 (Volts)	RAS Average	σ	Conc g/m ³
0	0.247	0.256	0.049	0.184	0.10	.01
1.67	3.077	0.947	3.416	2.480	1.09	.16
3.33	3.524	1.391	3.600	2.838	1.02	.18
5.00	3.282	2.021	3.258	2.853	0.59	.18
6.67	3.055	2.338	2.904	2.766	0.31	.17
8.33	2.823	2.348	2.748	2.640	0.21	.17
10.00	2.604	1.664	2.726	2.331	0.47	.15
11.67	2.326	1.679	2.241	2.142	0.33	.13
13.33	2.064	1.640	2.318	2.007	0.28	.13
15.00	1.789	1.420	2.047	1.752	0.26	.11
16.67	1.525	1.430	1.774	1.576	0.14	.10
18.33	1.606	1.342	1.520	1.498	0.11	.09
20.00	1.298	1.284	1.379	1.320	0.04	.08
21.67	1.144	1.081	1.210	1.145	0.05	.07
23.33	1.122	0.998	1.176	1.099	0.07	.07
25.00	1.049	0.820	0.847	0.905	0.10	.06
26.67	1.008	0.752	0.849	0.870	0.11	.05
28.33	0.856	0.735	0.808	0.800	0.05	.05
30.00	0.747	0.630	0.725	0.700	0.05	.04
31.67	0.688	0.696	0.654	0.679	0.02	.04
33.33	0.698	0.688	0.624	0.670	0.03	.04

APPENDIX A2

ROSCO FOG FLUID IN 1 M³ CHAMBER

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS 3 (Volts)	RAS Average	σ	Conc g/m ³
0	1.796	2.267	1.883	1.980	0.20	.12
1.67	3.233	0.544	3.250	2.341	1.27	.14
3.33	2.638	1.835	2.586	2.612	0.62	.16
5.00	2.218	2.255	2.587	2.353	0.17	.15
6.67	2.526	2.262	2.343	2.283	0.10	.15
8.33	2.289	2.201	2.594	2.460	0.18	.15
10.00	2.467	2.133	2.518	2.373	0.17	.15
11.67	2.281	2.064	2.332	2.226	0.12	.14
13.33	2.221	2.001	2.213	2.145	0.10	.13
15.00	2.169	1.955	2.138	2.087	0.09	.13
16.67	2.160	1.928	2.033	2.044	0.12	.13
18.33	2.111	1.874	1.999	1.994	0.10	.13
20.00	2.018	1.835	1.899	1.917	0.08	.12
21.67	1.984	1.789	1.927	1.900	0.08	.12
23.33	1.920	1.755	1.845	1.840	0.07	.12
25.00	1.866	1.716	1.791	1.791	0.06	.11
26.67	1.838	1.676	1.806	1.773	0.07	.11
28.33	1.784	1.637	1.769	1.730	0.07	.11
30.00	1.747	1.637	1.769	1.730	0.07	.11
31.67	1.676	1.567	1.652	1.632	0.05	.10
33.67	1.667	1.515	1.615	1.600	0.06	.10

APPENDIX A3

DECANOL IN 1 M³ CHAMBER

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS 3 (Volts)	RAS Average	σ	Conc. g/m ³
0	0.458	0.791	0.969	0.739	0.21	.05
1.67	2.648	0.437	3.402	2.162	1.26	.14
3.33	2.562	1.681	2.660	2.301	0.44	.14
5.00	2.326	1.745	2.565	2.212	0.34	.14
6.67	2.408	1.979	2.118	2.159	0.16	.14
8.33	2.379	1.979	2.118	2.159	0.16	.14
10.00	2.316	1.950	2.182	2.149	0.19	.13
11.67	2.206	1.879	2.186	2.090	0.15	.13
13.33	2.172	1.838	2.091	2.004	0.17	.13
15.00	2.047	1.769	1.977	1.931	0.11	.12
16.67	1.928	1.700	1.913	1.847	0.10	.12
18.33	1.806	1.711	1.838	1.785	0.05	.11
20.00	1.781	1.645	1.698	1.708	0.06	.11
21.67	1.723	1.613	1.620	1.652	0.05	.10
23.33	1.657	1.569	1.559	1.595	0.04	.10
25.00	1.586	1.503	1.559	1.595	0.04	.10
26.67	1.554	1.469	1.476	1.500	0.04	.09
28.33	1.493	1.420	1.406	1.440	0.04	.09
30.00	1.454	1.381	1.419	1.418	0.03	.09
31.67	1.384	1.359	1.359	1.367	0.01	.09
33.33	1.366	1.300	1.323	1.297	0.07	.08

APPENDIX A4

PROPYLENE GLYCOL IN 1 M³ CHAMBER

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS 3 (Volts)	RAS Average	σ	Conc (g/m ³)
0	1.320	0.566	2.399	1.428	.75	.089
1.67	1.940	0.376	1.876	1.397	.72	.087
3.33	1.393	0.578	1.877	0.949	.34	.059
5.00	0.791	0.666	0.564	0.674	.09	.042
6.67	0.603	0.493	0.244	0.446	.15	.028
8.33	0.373	0.305	0.186	0.288	.08	.018
10.00	0.305	0.234	0.188	0.242	.05	.015
11.67	0.254	0.134	0.151	0.180	.05	.011
13.33	0.188	0.085	0.105	0.126	.04	.008
15.00	0.095	0.076	0.044	0.072	.02	.004
16.67	0.046	0.063	0.032	0.047	.02	.003
18.33	0.034	0.059	0.027	0.033	.02	.002
20.00	0.032	0.049	0.019	0.033	.02	.002
21.67	0.022	0.032	0.019	0.014	.01	.002
23.33	0.019	0.024	0.017	0.020	.00	.001
25.00	0.019	0.022	0.017	0.020	.00	.001

APPENDIX A5

DODECANOL 1st RUN IN CLOCHE (T= 24 °C)

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS (Average)	Concentration (mg/m3)	Conc/Diss xg/m3/g diss
0	0	0	0	0	0
1	0	0	0	0	0
2	0	0	0	0	0
3	.0597	0.661	0.63	0.039	0.684
4	2.108	1.074	1.59	0.099	1.73
5	1.794	1.342	1.57	0.098	1.70
6	2.252	2.137	2.19	0.137	2.39
7	2.033	1.982	2.01	0.125	2.18
8	1.923	1.747	1.84	0.115	1.99
9	1.554	1.407	1.48	0.092	1.61
10	1.303	1.030	1.17	0.073	1.27
11	1.073	0.769	0.93	0.058	1.00
12	0.854	0.678	0.77	0.048	0.83
13	0.759	0.637	0.71	0.045	0.77
14	0.654	0.569	0.61	0.038	0.66
15	0.578	0.522	0.55	0.034	0.60
16	0.534	0.471	0.50	0.030	0.52
17	0.453	0.425	0.44	0.027	0.48

APPENDIX A6

DODECANOL 2nd RUN IN CLOCHE (T=21.5 °C)

TIME (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS Average	Conc (g/m ³)	Conc/Diss (mg/m ³ /g diss)
0	0.005	0.000	0.002	00	0.000
1	0.005	0.000	0.002	0.000	0.00
2	0.005	0.000	0.002	0.000	0.00
3	1.630	0.683	1.157	0.072	2.10
4	2.526	1.720	2.123	0.133	3.85
5	2.733	1.796	2.265	0.142	4.10
6	1.645	1.459	1.552	0.097	2.82
7	0.831	1.196	1.014	0.063	1.84
8	0.754	0.610	0.682	0.043	1.24
9	0.664	0.603	0.633	0.040	1.15
10	0.739	0.771	0.755	0.047	1.37
11	0.910	0.942	0.926	0.058	1.68
12	0.983	0.891	0.937	0.059	1.70
13	0.876	0.749	0.813	0.051	1.47
14	0.727	0.591	0.659	0.041	1.20
15	0.591	0.500	0.545	0.034	0.99
16	0.532	0.442	0.487	0.034	0.88
17	0.483	0.395	0.439	0.027	0.80

APPENDIX A7

EMERY 3002 IN CLOCHE (T = 27 °C)

Time (min)	RAS 1 (volts)	RAS 2 (volts)	RAS (Aver)	Conc (mg/m ³)	Conc/Diss μg/m ³ /g diss
0	0.0	0.0	0.0	0.0	0.0
1	0.0	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0	0.0
3	2.07	3.11	2.59	0.16	1.35
4	2.89	3.31	3.10	0.19	1.61
5	3.21	3.84	3.53	0.22	1.83
6	2.93	3.83	3.38	0.21	1.76
7	1.67	2.27	1.97	0.12	1.02
8	1.67	1.53	1.60	0.10	0.83
9	1.49	1.28	1.39	0.87	0.72
10	1.38	1.16	1.27	0.08	0.66
11	1.31	1.18	1.25	0.08	0.65
12	1.23	1.14	1.18	0.07	0.62
13	1.21	1.09	1.15	0.07	0.60
14	1.23	1.10	1.16	0.07	0.60
15	1.16	1.21	1.18	0.07	0.61
16	1.20	1.07	1.13	0.07	0.60
17	1.18	1.03	1.11	0.70	0.58

APPENDIX A8

EMERY 3004 IN CLOCHE (T=24 °C)

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS Average	Concentration (g/m3)	Conc/Diss (mg/m3/g diss)
0	0.005	0.000	0.003	0.000	0.00
1	0.005	0.000	0.003	0.000	0.00
2	0.005	0.000	0.003	0.000	0.00
3	2.226	0.664	1.445	0.090	1.23
4	3.250	2.977	3.114	0.195	2.64
5	2.953	2.843	2.898	0.181	2.46
6	3.543	3.160	3.351	0.209	2.84
7	3.409	3.153	3.281	0.205	2.78
8	3.424	3.070	3.247	0.203	2.75
9	3.362	3.006	3.184	0.199	2.70
10	3.260	2.977	3.118	0.195	2.65
11	3.138	2.753	2.945	0.184	2.50
12	2.701	2.233	2.467	0.154	2.09
13	2.431	2.255	2.343	0.146	1.99
14	2.326	2.128	2.227	0.139	1.89
15	2.257	2.016	2.136	0.133	1.81
16	2.064	1.874	1.969	0.123	1.67
17	1.994	1.813	1.903	0.119	1.61

APPENDIX A9

DODECANOL 1st RUN IN CLOCHE (T = 39 °C)

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS Average	Conc g/m ³	Conc/Dissem mg/m ³ /g diss
0	.002	0.000	0.001	0.000	0.00
1	0.002	0.000	0.001	0.000	0.00
2	0.002	0.000	0.001	0.000	0.00
3	0.276	0.642	0.459	0.029	0.92
4	0.239	0.595	0.417	0.026	0.84
5	0.525	0.935	0.730	0.046	1.46
6	0.100	0.115	0.107	0.006	0.22
7	0.005	0.005	0.005	0.000	0.01

APPENDIX A10

DODECANOL 2nd RUN IN CLOCHE (T = 39 °C)

Time (minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS (Average)	Concentration (g/m ³)	Conc/Dissem mg/m ³ /g dissem
0	0.00	0.00	0.00	0.00	0.00
0.5	0.00	0.00	0.00	0.00	0.00
1.0	0.00	0.00	0.00	0.00	0.00
2.0	0.00	0.00	0.00	0.00	0.00
3.0	0.00	0.00	0.00	0.00	0.00
3.5	0.244	0.012	0.128	0.0080	0.257
4.0	0.532	0.395	0.464	0.0290	0.930
4.5	0.369	0.212	0.290	0.0182	0.582
5.0	0.408	0.073	0.240	0.0150	0.482
5.5	0.306	0.315	0.311	0.0194	0.624
6.0	0.364	0.173	0.268	0.0168	0.538
6.5	0.151	0.154	0.153	0.0095	0.304
7.0	0.093	0.286	0.189	0.0118	0.379
7.5	0.051	0.237	0.144	0.0090	0.289
8.0	0.022	0.139	0.081	0.0050	0.162
8.5	0.034	0.078	0.056	0.0035	0.113
9.0	0.149	0.146	0.148	0.0092	0.296
9.5	0.093	0.105	0.099	0.0062	0.198
10.0	0.020	0.054	0.037	0.0023	0.073
10.5	0.015	0.042	0.028	0.0018	0.056
11.0	0.066	0.054	0.060	0.0037	0.120
11.5	0.061	0.046	0.054	0.0034	0.109
12.0	0.027	0.017	0.022	0.0014	0.044
12.5	0.015	0.010	0.012	0.0008	0.024
13.0	0.024	0.005	0.015	0.0009	0.029
13.5	0.000	0.00	0.00	0.00	0.00
14.0	0.000	0.00	0.00	0.00	0.00

APPENDIX A11

DODECANOL 3rd RUN IN CLOCHE (T = 41 °C)

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS Average	Conc (g/m ³)	Conc/Dissem (mg/m ³ /g diss)
0	0	0	0	0	0
1	0	0	0	0	0
2	0	0	0	0	0
3	0.149	0.000	0.074	0.005	0.10
4	0.000	0.068	0.034	0.002	0.05
5	0.000	0.200	0.100	0.006	0.14
6	0.024	0.354	0.189	0.012	0.26
7	0.354	0.444	0.399	0.025	0.54
8	0.449	0.552	0.500	0.031	0.68
9	0.364	0.464	0.414	0.026	0.56
10	0.315	0.253	0.284	0.018	0.39
11	0.229	0.242	0.236	0.015	0.32
12	0.122	0.200	0.161	0.010	0.22
13	0.151	0.144	0.148	0.009	0.20
14	0.063	0.083	0.073	0.005	0.10
15	0.051	0.056	0.054	0.003	0.07
16	0.012	0.032	0.022	0.001	0.03
17	0.007	0.015	0.011	0.000	0.01

APPENDIX A12

EMERY 3004 IN CLOCHE (T = 36 °C)

Time (Minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS Average	Concentration (g/m ³)	Conc/Dissem mg/m ³ /g diss
0	0.002	0.000	0.001	0.000	0.00
1	0.002	0.000	0.001	0.000	0.00
2	0.002	0.000	0.001	0.000	0.00
3	0.212	0.232	0.222	0.014	0.14
4	0.178	0.002	0.090	0.006	0.05
5	0.000	0.000	0.000	0.000	0.00
6	0.000	0.256	0.128	0.008	0.08
7	0.212	1.191	0.702	0.044	0.43
8	0.464	1.232	0.848	0.053	0.52
9	0.037	1.064	0.551	0.034	0.34
10	1.113	1.066	1.090	0.068	0.67
11	1.064	0.983	1.024	0.064	0.63
12	0.949	0.861	0.905	0.057	0.55
13	0.703	0.715	0.709	0.044	0.43
14	0.576	0.661	0.619	0.039	0.38
15	0.539	0.581	0.560	0.035	0.34
16	0.549	0.576	0.562	0.035	0.34
17	0.547	0.505	0.526	0.033	0.32

APPENDIX A13

OCTANOL IN CLOCHE (T = 17 °C)

Time (minutes)	RAS 1 (volts)	RAS 2 (volts)	RAS (Average)	Concentration (mg/m3)	Conc/Diss g/m3/g diss
0	0	0	0	0	0
1	0	0	0	0	0
2	0	0	0	0	0
3	0.79	0.26	0.53	0.333	0.486
4	0.62	0.77	0.70	0.043	0.641
5	0.769	0.910	0.84	0.052	0.773
6	1.030	1.001	1.02	0.063	0.936
7	0.854	0.822	0.84	0.052	0.772
8	0.772	0.534	0.62	0.038	0.567
9	0.627	0.534	0.62	0.038	0.567
10	0.566	0.505	0.54	0.033	0.493
11	0.461	0.420	0.44	0.028	0.406
12	0.395	0.347	0.37	0.023	0.342
13	0.342	0.283	0.31	0.019	0.288
14	0.286	0.244	0.26	0.017	0.244
15	0.259	0.203	0.23	0.014	0.206
16	0.225	0.188	0.16	0.010	0.149

APPENDIX A14

n-DECANOL IN CLOCHE (T = 26 °C)

Time (minutes)	RAS 1 (Volts)	RAS 2 (Volts)	RAS (Average)	Concentration (mg/m ³)	Conc/Diss μg/m ³ /g dissem
0	0.000	0.000	0.00	0.00	0.00
1	0.000	0.000	0.00	0.00	0.00
2	0.000	0.000	0.00	0.00	0.00
3	1.664	0.076	0.87	0.54	0.87
4	1.681	1.203	1.44	0.90	1.45
5	1.303	2.230	1.77	0.11	1.76
6	1.288	1.105	1.20	0.07	1.20
7	1.047	0.968	1.01	0.06	1.01
8	0.971	0.896	0.93	0.06	0.94
9	0.849	0.793	0.82	0.05	0.83
10	0.778	0.764	0.77	0.05	0.76
11	0.664	0.603	0.63	0.40	0.64
12	0.517	0.481	0.50	0.03	0.50
13	0.469	0.430	0.45	0.03	0.45
14	0.395	0.400	0.40	0.03	0.40
15	0.276	0.256	0.26	0.20	0.32
16	0.254	0.256	0.25	0.20	0.26
17	0.227	0.192	0.21	0.01	0.21